Raff nsperg r, Linda

39b163

From: Hale, Mary
Sent: Monday, May 20, 2002 1:58 PM
To: Raffensperger, Linda
Subject: FW:

In annex

Please treat this ILL request as a RUSH.

Thanks,
Mary

The publication is:

Inorganic Colloid Chemistry
vol. 1
p 137 - 148 Ch 5 yr ?

Exp
5/20

Harry Boyer Weiser-author

-----Original Message----- 1616
From: Choi, Frank
Sent: Monday, May 20, 2002 1:28 PM
T : Hale, Mary
Subject: RE:

1933-38

```
This the extent of the information I have on the reference.

A copper colloid  which initiated plating directly was prepared according
to a
procedure suggested by Weiser,  "Inorganic Colloid  Chemistry", Vol. 1, p.
137.
In this preparation, 40 ml of 0.01 M CuSO.sub.4  was heated to 80.degree.
C. 10
ml of 0.5% H.sub.3 PO.sub.2 was added with stirring.
```

-----Original Message-----
From: Hale, Mary
Sent: Monday, May 20, 2002 1:06 PM
To: Choi, Frank
Subject: RE:

Do you have the page numbers and the year? The best approach at this time would be to put in a ILL because it will not be an easy task pulling this book out of the boxes we have in the annex. This is a big project and these books have been packed away for 2 years. There are approximately 35+ boxes with 25 books in each box. It could take longer for us to go through the boxes, then putting in a ILL request. Please let me know the dates and page numbers so we can try to get the pages for you by Wednesday.

Mary

-----Original Message-----
From: Choi, Frank
Sent: Monday, May 20, 2002 12:58 PM
To: Hale, Mary
Subject: RE:

I need to look at the reference for prior art now for an application that I am currently prosecuting. The reference was cited in a prior art reference which partially described a process for preparation of a colloidal inorganic salt and cited the reference but I need to see the reference to see the complete process.
Is there anyway I could get access without having to go throught the procedure below.

-----Original Message-----
From: Hale, Mary
Sent: Monday, May 20, 2002 12:38 PM

CHAPTER V

COLLOIDAL COPPER AND MERCURY

COLLOIDAL COPPER

Copper is obtained in the colloidal state as sol and gel, and in a highly dispersed form for use as a contact catalyst and as a condensing agent in organic chemistry. The preparation and properties of the sols will be considered first.

Formation of Copper Sols

As compared with silver sols, copper sols are in general more difficult to prepare and are less stable in the absence of protecting colloids. Accordingly most copper sols are protected.

Reduction without Protecting Colloids.—Gutbier[1] reduced a dilute solution of copper sulfate with hypophosphorous acid at a temperature of 70°–80°. The resulting reddish brown sol was so instable that it could not be dialyzed without coagulation. Meyer[2] added sodium hydrosulfite to a very dilute solution of copper sulfate and after gentle warming obtained a beautiful red copper sol. The preparation was not very stable, coagulating spontaneously on standing for some time at room temperature or on heating.

Barnard[3] allowed 5% copper sulfate to drop into a 50% solution of hydrazine hydrate until a deep golden color was obtained. If a well-cleaned glass article is placed in the reducing agent before adding the copper salt, a thin adhering film of metallic copper is deposited on which a thick film of the metal may be plated electrolytically. This is a satisfactory method of plating copper on glass.

Reduction with Protecting Colloids.—A hydrosol of copper is obtained by adding a weakly alkaline solution of stannous chloride to a solution of copper chloride in alkali citrate or tartrate. The resulting precipitate is peptized by washing, giving a reddish brown sol, the particles of which are a copper-stannic oxide adsorption

[1] Z. anorg. Chem., **32**, 355 (1902).
[2] Z. anorg. Chem., **34**, 60 (1903).
[3] Science, **66**, 330 (1927).

complex resembling purple of Cassius. As would be expected, the sol possesses the properties of the more hydrophilic colloid rather than those of the metal.

Copper sols result by reduction with hydrazine hydrate of a colloidal solution of copper hydroxide prepared by adding copper sulfate to a solution of sodium protalbinate or lysalbinate.[4] With high concentrations in the cold, a relatively instable blue sol results; but by heating a mixture containing not more than 25% copper and a small amount of ammonia, a highly stable sol, red by transmitted light and black by reflected light, is obtained. Evaporation of the liquid out of contact with air gives a solid red powder which is peptized by shaking with water. Red colloidal copper that can be peptized by water is obtained also by reduction with hydrogen at 200°, of copper oxide formed in the presence of sodium protalbinate or lysalbinate. If the instable blue sol mentioned above is coagulated by dilute sulfuric acid, copper-red flocks are obtained which may be washed in an atmosphere of carbon dioxide and dried in a vacuum. This red powder is peptized by dilute alkali, giving a blue sol once more.[5]

Copper sol also results by reduction of ammoniacal copper sulfate with hydrazine hydrate in the presence of gum arabic[6] or of island moss.[7]

A novel method of preparing a stable copper sol consists in suspending freshly prepared pure white cuprous chloride in a solution of 10% casein in 2% sodium hydroxide. After a time, a ruby-red to black-red sol results which is said to be useful as a ray filter since it transmits only red light of a definite wave length.[8]

Electrical Methods.—Relatively stable olive-green to brown-green hydrosols are readily prepared by passing an arc between copper wires under water, according to Bredig's method.[9] Burton[10] obtained a methyl alcosol by the Bredig method, but it was contaminated with carbon. With the oscillating arc a relatively pure copper etherosol and isobutyl alcosol were made by Svedberg (see page 162). The former was black and the latter greenish black in transmitted light.

[4] Paal and Leuze: Ber., **39**, 1550 (1900); Gerasimov and Matveev: J. Russ. Phys-Chem. Soc., **62**, 839 (1930).

[5] Paal and Amberger: Ber., **38**, 1398 (1905).

[6] Gutbier and Hofmeier: Z. anorg. Chem., **44**, 227 (1905).

[7] Gutbier and Sauer: Kolloid-Z., **25**, 145 (1919).

[8] German Pats., 383,098 and 325,957.

[9] Ehrenhaft: Anz. Akad. Wiss. Wien, **39**, 241 (1902); Sitzber. Akad. Wiss. Wien, **112**, 182 (1903); *cf.* Billitzer: Ber., **35**, 1933 (1902).

[10] Phil. Mag., (6) **11**, 472 (1906).

Composition and Properties of Copper Sols

Composition

Copper sols formed by Bredig's method have been shown by x-ray analysis to be coated with a layer of copper oxide.[11] Both hydroxide and oxide have been detected chemically in this sol, the ratio $Cu(OH)_2/CuO$ decreasing with the time of passing the arc and with increasing *p*H value of the solution.[12] The conductivity of copper sols is distinctly lower than that of either silver or platinum sols. Evans[13] obtained values of 0.30–0.50 mho/cc, which were less than that of the conductivity water. This was attributed to adsorption of ions by the gelatinous copper hydroxide on the surface of the particles. According to Murray,[14] the conductivity of Bredig's copper sols is probably due largely to the saturated solution of copper hydroxide formed during the arcing process.

The positive charge on the particles of Bredig sols is due to preferential adsorption of copper ions by the oxide or hydroxide layer surrounding the particles. The hydroxyl ions are the contra ions which constitute the diffuse outer portion of the double layer.

No definite information is available concerning the composition and constitution of the relatively impure protected sols formed by reduction processes.

Stability of Sols

Effect of Radiations.—As already noted, chemically prepared copper sols formed in the absence of protecting colloids are quite instable. The Bredig sols are fairly stable at ordinary temperatures, but they are easily coagulated by the addition of electrolytes, by subjecting them to x-rays or the β-rays from radium, and by raising the temperature. Crowther[15] attributes the discharging action of the radiation to negative ions produced in the dispersing solvent by the ionizing agents. The action is therefore confined to positively charged sols. Moreover, since the negative ion produced by the ionizing agent appears to be the only active agent in the process, the effect is independent of the source of the ionizing radiation.

[11] Freundlich: Ber., **61**, 2219 (1928).
[12] Podrouzek: Chem. Listy, **20**, 403 (1926).
[13] Trans. Faraday Soc., **24**, 409 (1928).
[14] J. Chem. Soc., 1235 (1928).
[15] Phil. Mag., (7) **7**, 86 (1929); Crowther and Fairbrother; **4**, 325 (1927); *cf.* Bhatnagar, *et al.*; Z. Physik, **56**, 684 (1929).

Effect of Heat.—For a colloid like Bredig's copper sol to be stable, the particles must be sufficiently small that the Brownian movement keeps them from settling under the influence of gravity, and the charge on the particles must be sufficiently large that collisions do not result in coalescence of the particles to form larger aggregates. The mutual repulsion of oppositely charged particles does not come in until the particles are quite close together. Since it is now generally recognized that the outer layer of the electrical double layer is quite diffuse and may be several molecular diameters in thickness, the close approach of two particles will result in an overlapping of the outer layers so that the particles will possess an effective charge relative to one another and consequently will repel one another. But if the charge is sufficiently low or the Brownian movement sufficiently intense, the particles may touch and form an agglomerate in spite of the repulsion. One would expect the frequency of the effective collisions to be increased by lowering the charge on the particles by the addition of electrolytes or by increasing the intensity of the Brownian movement. The effect of electrolytes on the particle charge of hydrosols and hence on their stability has received extended study, and the effect of temperature alone on organosols has been considered by Svedberg and Inouye.[16] Recent investigations by Burton and his pupils[17] on a Bredig copper hydrosol show that, if samples of the sol are maintained at different high temperatures for a definite time interval, there exists one temperature below which the samples do not coagulate in a given time and above which they do coagulate. This temperature has been termed the "coagulation temperature" for the sol.

In the actual experiments the samples of sol were placed in a copper tube and sealed in a glass tube which was immersed in an electrically heated bath for a given time interval. Observations were made of the presence or absence of coagulation 24 hours after heating. Some results are given in Fig. 22. It is apparent that coagulation may be brought about by temperature alone. Moreover, the coagulation temperature decreases with increasing time of heating when the particle charge in each case is the same. Since the curve becomes asymptotic with the axis of time, the sol might be expected to remain stable indefinitely at room temperature. Finally, it was found that, by varying the charge on the particles by adding different amounts

[16] Kolloid-Z., 9, 153 (1911).

[17] Reid and Burton: J. Phys. Chem., 32, 425 (1928); Deacon: 34, 1105 (1930); Burton and Deacon: Colloid Symposium Monograph, 6, 77 (1928).

of potassium chloride, the coagulation temperature decreases with decreasing charge for the same time of heating.

In every case, heating the sol speeds up the process of coagulation so that eventually all the heated samples coagulate. The reason is that multiple particles are formed during the heating process, the more the higher the temperature, and that these agglomerates act as coagulation nuclei for smaller particles.[18]

The reason for the horizontal position of the curve in Fig. 22 is

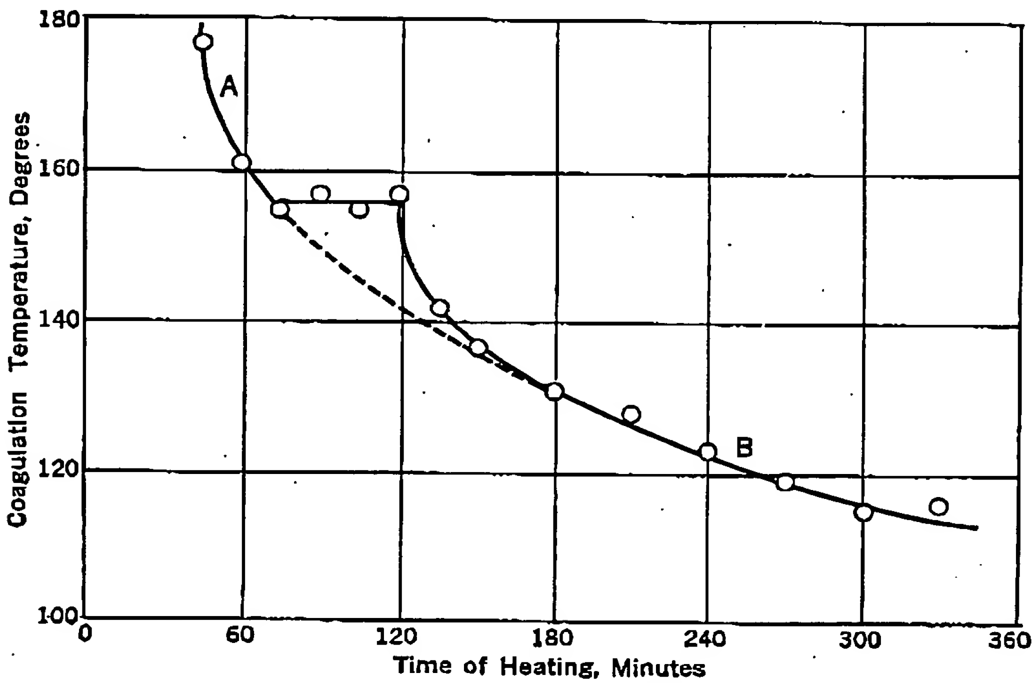

FIG. 22.—Effect of heat on the coagulation time of colloidal copper.

not at once apparent. It is suggested that at a temperature of 155° the cupric oxide or hydroxide on the particles is reduced to the cuprous state, thus disturbing the charge on the particles. If this be true, it is not obvious why the portions *A* and *B* apparently belong to the same smooth curve.

Effect of Electrolytes and Non-electrolytes on Organosols.—An alcosol of copper prepared by Bredig's method is sensitized and ultimately coagulated[19] by solutions of salts in various organic media miscible with alcohol, such as acetone, ether, and glycerin. The order of precipitating power of the salts is: lithium chloride < ammonium bromide < strontium chloride < mercuric chloride < aluminum chloride, which is the same as for a negative hydrosol. This

[18] Wiegner: Kolloid-Z., 8, 227 (1911); Galecki: Z. anorg. Chem., 74, 174 (1912); Müller: Kolloid-Beihefte, 26, 257 (1928).

[19] Yajnik, Goyle, and Bhan: J. chim. phys., 27, 386 (1930).

indicates that copper dispersed in ethyl alcohol is negatively charged. For a zinc sol in acetone, the cation is likewise the precipitating ion, the order of precipitating power of salts being: lithium chloride < sodium iodide < calcium nitrate < mercuric chloride < antimony trichloride. The coagulating action is due both to the lowering of the charge on the particle by the electrolyte and to the change in the solvation of the particle in the presence of the added non-electrolyte.[20]

Color

Like silver, colloidal copper exists in a wide variety of colors. Thus Paal and Steyer[21] obtained sols of the following colors: reddish brown, blue, ruby red, brown, olive, and green. Copper is used in place of gold in the preparation of a cheaper grade of ruby glass. In true copper ruby glass the particles are of ultramicroscopic dimensions; in opaque copper-red hematinon, they are microscopically visible; and in aventurine glass, they exist as spangles visible to the naked eye. From analogy with gold ruby glass one would expect the color of copper ruby glass to be due to colloidal copper. Williams[22] subscribes to this view, but Seger[23] attributes the color to colloidal cuprous oxide or copper silicate. Stokes[24] argues against the red color being due to colloidal copper on the ground that the most finely divided copper is blue; but his argument is not valid since it is the coarser particles which are blue. It is difficult to distinguish between colloidal copper and cuprous oxide in glass; but if the color is due to a copper silicate in solution, the glass should not scatter light as would a colloidal coloring agent.

Pharmacological Action

As already noted (see page 133), both colloidal silver and mercury are better bactericides than colloidal copper. The germicidal action of Bredig copper sol has been shown to be due exclusively to copper ions from cupric oxide and cupric carbonate formed in the presence of atmospheric gases.[25] Colloidal copper has been suggested

[20] *Cf.* Weiser and Mack: J. Phys. Chem. 34, 101 (1930).
[21] Kolloid-Z., 30, 88 (1922).
[22] Trans. Am. Ceram. Soc., 16, 284 (1914).
[23] "Collected Writings," 2, 731 (1902); Zulkowski: J. Soc. Chem. Ind., 16, 441 (1897).
[24] "Mathematical and Physical Papers," 4, 245 (1904).
[25] Kusunoki: J. Biochem. (Japan) 3, 1 (1923).

for use in the treatment of cancer, but it has little apparent destructive action on tumor tissue.[26]

Solid Forms of Colloidal Copper

Copper Gel.—By electrolyzing in the cold a neutral or feebly basic 10% solution of copper acetate, Schutzenberger[27] obtained an extremely brittle, bronze-colored deposit which was very readily oxidized, had a higher electrical resistance than copper, and a specific gravity of 8 to 8.2, which is appreciably lower than that of the metal in mass. The deposit became like ordinary copper if heated rapidly to 100° or allowed to stand for some time in contact with dilute sulfuric acid. Schutzenberger believed this preparation to be an allotropic form of copper, and Benedicks[28] regarded it as a solid solution of acetic acid in ordinary copper. Briggs[29] showed, however, that the deposit was in reality a gel of the normal metal consisting of finely divided particles which were prevented from agglomerating into a dense mass by adsorption of a protecting film of gelatinous hydroxide or basic acetate from the partly hydrolyzed solution.

Briggs electrolyzed solutions of copper propionate, acetate, or formate in the presence of gelatin and obtained a finely divided deposit of gelatin-copper which underwent a striking "development" on immersion in a copper salt of a weak acid such as the acetate or propionate. The color changed from the original pale brown, through reddish purple, purple, and finally blue. The blue coloration was attributed to adsorption from the solution by the colloidal copper, of hydrous copper oxide or hydroxide, giving a colloidal copper-copper oxide adsorption complex similar to the gold-stannic oxide mixture, purple of Cassius.

Organic Condensing Agent.—Colloidal copper for use as a condensing agent is prepared by shaking zinc dust through a fine sieve into a thoroughly agitated, cold, saturated copper sulfate solution. The precipitate of finely divided copper is treated with dilute hydrochloric acid to remove any zinc, and finally is washed thoroughly with water.[30]

[26] Weil: J. Am. Med. Assoc., **61**, 1034 (1913).
[27] Compt. rend., **86**, 1265, 1398 (1878).
[28] Metallurgie, **4**, 33 (1907).
[29] J. Phys. Chem., **17**, 281 (1913).
[30] Cohn: "Arbeitsmethoden organisch-chemische Laboratorium," 360 (1903).

COLLOIDAL MERCURY

The importance of mercury and its salts as therapeutic agents was not recognized until comparatively recent times, although Parcelsus, in the sixteenth century, introduced widely the use of colloidal mercury as a medicine in the form of blue ointment, a preparation formed by triturating mercury with fats. Mercury in bulk has comparatively little therapeutic action. Its efficacy in the colloidal state is probably due to the presence of more or less oxide which yields mercury ions, the real bactericide. In recent times, investigations on the colloidal metal has been concerned largely with the formation of hydrosols which may be used as antiseptics and disinfectants.

Formation of Mercury Sols

Reduction Methods

Sols formed by reduction methods, even under the most favorable conditions, are relatively instable in the absence of suitable protecting colloids. Thus Weinmayr[31] reduced a solution of mercuric chloride by hydrogen peroxide in the presence of a gold nuclear solution. Although this might be expected to yield a stable sol with small, relatively uniform particles, the preparation soon became cloudy and precipitated.

Lottermoser's Sol.—A satisfactory stable sol was first prepared by Lottermoser[32] by reduction of mercurous salts with stannous salts. By using 5–10% solutions of stannous nitrate and mercurous nitrate, containing enough nitric acid to prevent precipitation, a clear, red-brown sol results which soon precipitates in the strong acid solution. By neutralizing the acid with sodium hydroxide, a fine black mass is thrown down from which the excess electrolyte is removed by filtration. The precipitate is readily peptized by water and retains this property even after washing with alcohol[33] and drying in vacuum.

From the point of view of ease of preparation and stability, Lottermoser's preparation has not been improved upon.[34] It is in reality a mercury "purple" in which the protecting agent is the relatively inert and highly stable hydrous stannic oxide.

[31] German Pat., 217,724 (1910).

[32] J. prakt. Chem., (2) 57, 484 (1898); 72, 39 (1915); U. S. Pat., 685,477 (1901).

[33] *Cf.* Schneider: Ber., 25, 1281 (1892).

[34] *Cf.* Feick: Kolloid-Z., 37, 260 (1925).

Paal's Sol and Similar Preparations.—Paal[35] reduced mercuric oxide with hydrazine hydrate in the presence of his protecting sodium protalbinate and lysalbinate, in much the same way as he prepared the corresponding silver and copper sols. Other protecting colloids which give more or less satisfactory preparations using suitable reducing agents are plant extracts,[36] gelatin,[37] dextrin, gums and gluten,[38] soap,[39] casein,[40] and glycogen.[41]

Rhythmic bands of mercury in the form of drops about 0.0001 cm in diameter result on allowing dilute mercurous nitrate to diffuse into 3% agar containing 0.5% sodium formate.[42]

Mechanical Methods

If a very fine stream of mercury is ejected forcibly against a glass wall under water containing $2.5 \times 10^{-3}\ N$ potassium citrate, only a very dilute, coarsely dispersed sol is obtained.[43] On the other hand, if the dilute citrate solution is forced to rise through mercury, thin mercury lamellae are produced when the surface of the metal is reached, and the bursting of these lamellae gives a sol containing droplets smaller than in any other mercury sol yet prepared. Similar results are obtained by shaking mercury with the dilute citrate solution, the optimum concentration for making the strongest sols being between 2 and $7 \times 10^{-3}\ N$. After the larger particles settle out, the resulting reddish brown sol is highly stable. Nordlund reports that a sol formed by shaking shows no trace of coagulation after standing a month. Other dilute solutions such as sodium tartrate and ammonium sulfate may be substituted for citrate, but the resulting sols are much less stable.

More or less stable sols can be formed by shaking mercury with other liquids such as ether and turpentine; and solid or semi-solid sols result by triturating with sulfur, antimony sulfide, sugar, grease, etc.

[35] Ber., **35**, 2219 (1902); *cf.* Hoffmann: German Pat., 185,600 (1907); Amberger: Kolloid-Z., **8**, 88 (1911); **18**, 97 (1916); German Pats., 178,520 (1905); 186,061; 186,138 (1907).

[36] Gutbier and coworkers: Kolloid-Z., **19**, 33, 291 (1916); **20**, 83, 123 (1917); **25**, 97 (1919).

[37] Lobry de Bruyn: Rec. trav. chim., **19**, 240 (1900); Westgren: Z. physik. Chem., **83**, 151 (1913); Feick: Kolloid-Z., **37**, 257 (1925).

[38] German Pat., 286,414 (1915).

[39] Roth: German Pat., 228,139.

[40] Busch: German Pat., 189,480 (1907).

[41] Hugounenq and Loiseleur: Compt. rend., **182**, 851 (1926).

[42] Davis: J. Am. Chem. Soc., **39**, 1312 (1917).

[43] Nordlund: Kolloid-Z., **26**, 121 (1920).

A sol which required 1.5 months to settle completely was prepared by grinding mercury for a long time with glucose and dissolving out the glucose with water.[44]

Pharmaceutical Preparations.—In Table XXIII are listed some of the more important therapeutic preparations of colloidal mercury referred to in the United States, and British pharmacopoeias. In every case the mercury is reduced to the colloidal state by trituration.

TABLE XXIII

PHARMACEUTICAL PREPARATIONS OF COLLOIDAL MERCURY

Name	Dispersion medium	Colloidal Hg in %	Use
Mercury ointment (blue ointment)	Suet, lard, and vaselin	30	Against cutaneous parasites
Mercury ointment (Scott's dressing)	Lard and camphor	12	In synovitis
Mercury ointment	Lard and suet	50	For inunction
Mercury mass (blue mass)	Licorice root and confection of roses	33	Similar to calomel
Mercury plaster	Lead plaster base	33	Against glandular enlargements
Mercury with chalk	Chalk and honey	38	In infantile paralysis

Thermal Methods

If mercury is boiled vigorously and the vapors conducted into water containing ice, a brownish red sol is obtained[45] which coagulates within 24 hours. The simultaneous condensation of water and mercury vapor to give sols according to the method of Roginsky and Schalnikoff[46] has been described in Chapter I.

Electrical Methods

The Bredig method for the preparation of a stable mercury sol was first used successfully by Billitzer,[47] who employed a rigid cathode of zinc, cadmium, or iron on which a layer of mercury was electroplated.

[44] Von Weimarn and Utzino: Alexander's "Colloid Chemistry," 1, 659 (1926).
[45] Nordlund: Kolloid-Z., 26, 121 (1920); Gutbier: Z. anorg. Chem., 158, 99 (1926).
[46] Kolloid-Z., 43, 67 (1927); Tomaschewsky: 54, 79 (1931).
[47] Ber., 35, 1929 (1902).

The resulting sol was relatively pure, but the metal content was low. A sol may be formed by passing an arc between two fine streams of mercury under water.[48] To obtain a high degree of dispersion, it is apparently important to employ a low current density.

Nordlund[49] prepared concentrated sols using either the direct- or oscillating-current arc under conductivity water between one flowing and one stationary mercury electrode. The former was a stream of mercury 0.4–0.8 mm in diameter, and the latter was a pool of the element in the bottom of a flask. The distance between the electrodes was regulated so that a current of 2.8 amperes at 220 volts was obtained. The temperature was kept down by passing ice water through a coil immersed in the water. With the direct current, stable 4% mercury sols, and with the oscillating current, 0.5% mercury sols, were obtained at the rate of 8 minutes for each 100 cc of water.

A salve similar to blue ointment may be prepared by passing an arc between mercury electrodes immersed in molten vaselin, lanolin, etc.[50] An isobutyl alcosol prepared by means of an oscillating discharge at $-80°$ was quite instable, coagulating in an hour or two.

McCoy and Moore[51] electrolyzed a solution of tetramethyl ammonium chloride in absolute alcohol at a mercury cathode. The resulting amalgam decomposed violently when treated with water, giving highly dispersed, black colloidal mercury in the form of a hydrous precipitate.

Properties of Mercury Sols

Composition and Stability.—Like copper, but unlike silver and gold, the particles in an unprotected mercury sol are usually positively charged. This is probably due to the presence on the particles of a film of oxide which adsorbs mercury and hydrogen ions sufficiently strongly that the inner portion of the double layer is positive. In the presence of the strongly adsorbed citrate ion, the particles are negatively charged. The charge on the protected colloids depends on the nature of the protecting agent. Thus the Lottermoser sol is negative since the protector is hydrous stannic oxide.

The oxide content of colloidal mercury preparations varies widely.

[48] Svedberg: "Colloid Chemistry," 1st ed., 40 (1924); Egger: German Pat., 218,873 (1910).

[49] Kolloid-Z., **26**, 121 (1920); *cf., also*, Zavrieff: Z. physik. Chem., **87**, 507 (1914).

[50] Schereschewsky: German Pat., 153,995 (1904).

[51] J. Am. Chem. Soc., **33**, 279 (1911).

In Bredig sols prepared by Laird,[52] an average of 37% of the mercury was found to be in the form of oxide. As already noted, the varying therapeutic action of colloidal mercury in its various forms is probably due largely to mercury ion derived from oxide in the sol.

Color.—Highly dispersed mercury sols are in general reddish brown, whereas those containing larger drops are gray. With decreasing particle size from 300 mμ to 80 mμ in diameter, Feick[53] observed the following color by transmitted light: gray, grayish blue, grayish violet, reddish brown, orange, and yellow; and by reflected light: very dark brown, sandstone red, Venetian red, loam-brown, field-gray, green, bluish green, greenish blue and petroleum-like blue, and indigo. The observed colors are in good agreement with what would be expected from Mie's theory (see page 78). This furnishes a good test of the applicability of the theory, since the liquid particles of mercury sols are probably more nearly spherical than are the solid particles in most sols.

[52] J. Phys. Chem., **31**, 1034 (1927).
[53] Feick: Kolloid-Z., **37**, 257 (1925); Ann. Physik, (4) **77**, 673 (1925).

1105/20

STIC-ILL

From:	Choi, Frank
Sent:	Monday, May 20, 2002 1:47 PM
T :	STIC-ILL
Subject:	RE: ILL_Order

396311

Here is the relevant pages

Weiser, "Inorganic Colloid Chemistry ", vol. 1, pp. 1-5, 137-143, John Wiley &
Sons, .COPYRGT.1933.

already rec'd

-----Original Message-----

From:	Choi, Frank
Sent:	Monday, May 20, 2002 10:57 AM
T :	STIC-ILL
Subject:	ILL_Order
Importance:	High

Frank Choi
AU 1616
CM1-2D16
Serial No. 09/811,610
308-0067

Need to see copy of Inorganic Colloid Chemistry
Weiser, Harry Boyer
QD 549,w4i
Supposedly it is annex, however, it appears to be in one of the boxes and could not be readily accessed.

GM 5/22

NO

LC LHL 5/23

THE COLLOIDAL ELEMENTS

CHAPTER I

THE FORMATION OF COLLOIDAL ELEMENTS

Substances are obtained in the colloidal state either by gathering smaller particles, molecules, or atoms into particles of colloidal dimensions or by subdividing material in mass into particles of colloidal dimensions. The first process is called condensation or precipitation, and the second process, dispersion. Condensation methods are by far the most important in the preparation of colloidal elements, and they will be considered first.

Condensation Methods

The elements are most commonly obtained in the colloidal state in the form of what are known as colloidal solutions or sols, in which the element in a high state of subdivision is dispersed in a liquid or solid medium. Two general methods of preparing sols of the elements are widely used: the first involves precipitation as a result of chemical reaction in solution or of replacement of solvent; and the second consists in the condensation of vapors, especially of metallic vapors formed in the electric arc.

Precipitation from Solution

The first systematic study of the form in which substances precipitate as a result of reactions in solution was made by von Weimarn,[1] who emphasized that substances pass through the colloidal state during the precipitation process.

Von Weimarn's Theory.—Von Weimarn points out that precipitation from solution takes place in two stages: the first, in which the molecules in solution condense to crystalline nuclei; and the second, which is concerned with the growth on the nuclei as a result of diffusion.

[1] "Zur Lehre von den Zuständen der Materie" (1914).

The initial rate of precipitation, W, is expressed in von Weimarn's equation

$$W = K\frac{Q - L}{L} = K\frac{P}{L}$$

where K is a constant; Q, the total concentration of the substance that is to precipitate; and L, its solubility. $Q - L = P$ is the absolute supersaturation, and P/L is the percentage supersaturation.

The velocity of growth, V, on nuclei is given by the Nernst-Noyes equation

$$V = \frac{D}{S} \cdot O \cdot (Q - L)$$

where D is the diffusion coefficient; S, the thickness of the adherent film; O, the extent of surface; and Q and L have the same significance as above.

In actual practice, W cannot be measured, and V either cannot be measured at all or only with greatest difficulty. Accordingly, von Weimarn introduced what he termed the "precipitate form coefficient," N, which is related to the mean magnitude of the single crystals in gram molecules Gm, by the expression

$$Gm \times N = \text{constant}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression

$$N = \frac{P}{L}$$

which means that, in the simplest case, the form of a precipitate is determined exclusively by the prevailing percentage supersaturation at the moment the precipitation starts. If this is approximately true, then for the substances x, y, and z

$$N_x = \frac{P_x}{L_x}; \quad N_y = \frac{P_y}{L_y}; \quad \text{and} \quad N_z = \frac{P_z}{L_z}$$

Now if the mean size in gram molecules of the particles in the several precipitates is to be the same, that is, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}$$

This is the simplest form of von Weimarn's law of corresponding states for the precipitation process.

As would be expected, the simple formulation is seldom applicable quantitatively, since in most cases a number of factors other than percentage supersaturation influence the value of N and hence the mean particle size; and the magnitude of these factors is, in general, different with different substances. To take care of these several factors, von Weimarn introduces a multiplier, J, into the equation for N, which now becomes

$$N = J\frac{P}{L}$$

But as a rule the value of J is not the same for different substances; hence the expression for von Weimarn's law of corresponding states becomes

$$J_x\frac{P_x}{L_x} = J_y\frac{P_y}{L_y} = J_z\frac{P_z}{L_z}$$

in which J_x, J_y, and J_z are specific variable multipliers, "the product of all other factors in addition to P/L which influence the crystallization process. These factors must be expressed in abstract numbers equivalent to that for P/L."[2] This means simply that von Weimarn's law becomes quantitative and generally applicable by using variable multipliers which may include an indefinite number of unevaluated variables. Among the several factors which are lumped together in the variable multipliers are: the effect of the viscosity of the reaction medium, the variation in solubility with the size of the primary particles, polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, the specific tendency to grow on nuclei, etc.

Fortunately, in a number of cases the von Weimarn formulation may be used to advantage in its simplest form. This is true under the following conditions: (1) if the factors influencing the precipitation process which are lumped together in von Weimarn's J are relatively unimportant as compared with the prevailing P/L value at the moment of precipitation; (2) if the factors included in J are significant but are approximately equal for the precipitation of the two or more substances under consideration.

In cases where the J factors may be disregarded, von Weimarn's

[2] Von Weimarn: Kolloid-Beihefte, 18, 48 (1923).

equation $N = J \cdot P/L$ means that the nature of the precipitate is determined by the percentage supersaturation and the solubility prevailing at the moment precipitation begins. Thus, with a given value of P, a very soluble substance will form slowly and deposit relatively large crystals, whereas, for the same value of P, a quite insoluble substance will precipitate rapidly in a finely divided flocculent or gelatinous state. Since the metals are so insoluble it follows that in general they can be caused to precipitate from solution in a finely divided form. The problem in their colloid synthesis is to prevent the growth or agglomeration of the primary particles into secondary aggregates which are so large that they settle out under the influence of gravity. In general, sol formation is accomplished the more readily, the lower the solubility of the precipitating substance and the higher the dilution. In actual practice, the methods employed involve precipitation as finely divided particles which are prevented from growing beyond a certain size or from agglomerating into large aggregates by means of suitable strong adsorption, including protecting colloids, or by keeping the concentration of agglomerating agents low by choice of reaction or by dilution.[3] The types of chemical reactions which have been found to yield sols of the elements are reduction, oxidation, and dissociation.

Reduction without Protecting Colloids.—Reduction with or without the use of protecting colloids is by far the most important chemical reaction for preparing the elements in the sol state. Noteworthy examples are the preparation of gold sol by reduction with hydrogen peroxide[4] and the reduction of silver oxide by hydrogen.[5] The respective reactions may be represented as follows:

$$2HAuCl_4 + 3H_2O_2 \rightarrow 2Au + 8HCl + 3O_2$$

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

Both these reactions have received extended study and throw much light on the following factors as they influence sol formation: concentration of reactants, presence of nuclei, purity of solutions, and the nature of the containing vessel. All these several factors will be considered in detail in the chapters dealing specifically with colloidal gold and colloidal silver.

Elements that have been obtained in the sol state by reduction

[3] *Cf.* Bancroft: J. Phys. Chem., **18**, 556 (1914).
[4] Dörinckel: Z. anorg. Chem., **63**, 344 (1909).
[5] Kohlschütter: Z. Elektrochem., **14**, 49 (1908); Kolloid-Z., **12**, 285 (1913).

processes include gold, silver, platinum, palladium, iridium, rhodium, ruthenium, osmium, mercury, bismuth, copper, selenium, and tellurium.

Reduction with Protecting Colloids.—The stability of colloidal dispersions may be greatly increased by precipitating the finely divided particles in the presence of hydrophilic or water-soluble colloids such as gelatin, tannin, gum arabic, casein, glue, starch, albumin, and the sodium salts of protalbinic and lysalbinic acids formed by the saponification of albumin. The stabilizing action is due to adsorption of the hydrophilic colloid by the colloidal particles. In many cases the protecting colloid plays the combined rôle of reducing and stabilizing agent. For example, highly stable gold and silver sols are obtained by reduction of solutions of salts of the respective metals with tannin or sodium protalbinate.

Oxidation.—The oxidation process which is most important in sol formation is the oxidation of hydrogen sulfide by sulfur dioxide. Since most of the sulfur is precipitated in the colloidal state, the reaction which takes place is usually represented by the equation:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The actual reaction, however, is much more complicated, leading to the formation of a number of the thionic acids as well as colloidal sulfur.[6] It is now known that the presence of small amounts of one or more of the thionic acids is essential to the formation of a stable sulfur hydrosol.[7]

Dissociation.—Dissociation processes are seldom encountered in the preparation of sols in liquid media. A noteworthy example is the thermal dissociation of nickel carbonyl in benzol with the formation of a brown to black benzosol of nickel. The dissociation may be represented as follows:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$ [8]

A number of salts can be caused to dissociate under such conditions that dispersions of the corresponding metals in a solid medium are formed. Thus Lorenz[9] showed that crystals of lead chloride, silver

[6] Wackenroder: Arch. Pharm., **48**, 272 (1840).

[7] Freundlich and Scholz: Kolloid-Beihefte, **16**, 234 (1922); Bassett and Durrant: J. Chem. Soc., 2919 (1931).

[8] Ostwald: Kolloid-Z., **15**, 204 (1914); Hatschek and Thorne: **33**, 1 (1923).

[9] Lorenz and Eitel: Z. anorg. Chem., **91**, 46, 57, 61 (1915); Kolloid-Z., **18**, 177. (1916)

CHAPTER V

COLLOIDAL COPPER AND MERCURY

COLLOIDAL COPPER

Copper is obtained in the colloidal state as sol and gel, and in a highly dispersed form for use as a contact catalyst and as a condensing agent in organic chemistry. The preparation and properties of the sols will be considered first.

Formation of Copper Sols

As compared with silver sols, copper sols are in general more difficult to prepare and are less stable in the absence of protecting colloids. Accordingly most copper sols are protected.

Reduction without Protecting Colloids.—Gutbier[1] reduced a dilute solution of copper sulfate with hypophosphorous acid at a temperature of 70°–80°. The resulting reddish brown sol was so instable that it could not be dialyzed without coagulation. Meyer[2] added sodium hydrosulfite to a very dilute solution of copper sulfate and after gentle warming obtained a beautiful red copper sol. The preparation was not very stable, coagulating spontaneously on standing for some time at room temperature or on heating.

Barnard[3] allowed 5% copper sulfate to drop into a 50% solution of hydrazine hydrate until a deep golden color was obtained. If a well-cleaned glass article is placed in the reducing agent before adding the copper salt, a thin adhering film of metallic copper is deposited on which a thick film of the metal may be plated electrolytically. This is a satisfactory method of plating copper on glass.

Reduction with Protecting Colloids.—A hydrosol of copper is obtained by adding a weakly alkaline solution of stannous chloride to a solution of copper chloride in alkali citrate or tartrate. The resulting precipitate is peptized by washing, giving a reddish brown sol, the particles of which are a copper-stannic oxide adsorption

[1] Z. anorg. Chem., 32, 355 (1902).
[2] Z. anorg. Chem., 34, 60 (1903).
[3] Science, 66, 330 (1927).

complex resembling purple of Cassius. As would be expected, the sol possesses the properties of the more hydrophilic colloid rather than those of the metal.

Copper sols result by reduction with hydrazine hydrate of a colloidal solution of copper hydroxide prepared by adding copper sulfate to a solution of sodium protalbinate or lysalbinate.[4] With high concentrations in the cold, a relatively instable blue sol results; but by heating a mixture containing not more than 25% copper and a small amount of ammonia, a highly stable sol, red by transmitted light and black by reflected light, is obtained. Evaporation of the liquid out of contact with air gives a solid red powder which is peptized by shaking with water. Red colloidal copper that can be peptized by water is obtained also by reduction with hydrogen at 200°, of copper oxide formed in the presence of sodium protalbinate or lysalbinate. If the instable blue sol mentioned above is coagulated by dilute sulfuric acid, copper-red flocks are obtained which may be washed in an atmosphere of carbon dioxide and dried in a vacuum. This red powder is peptized by dilute alkali, giving a blue sol once more.[5]

Copper sol also results by reduction of ammoniacal copper sulfate with hydrazine hydrate in the presence of gum arabic[6] or of island moss.[7]

A novel method of preparing a stable copper sol consists in suspending freshly prepared pure white cuprous chloride in a solution of 10% casein in 2% sodium hydroxide. After a time, a ruby-red to black-red sol results which is said to be useful as a ray filter since it transmits only red light of a definite wave length.[8]

Electrical Methods.—Relatively stable olive-green to brown-green hydrosols are readily prepared by passing an arc between copper wires under water, according to Bredig's method.[9] Burton[10] obtained a methyl alcosol by the Bredig method, but it was contaminated with carbon. With the oscillating arc a relatively pure copper etherosol and isobutyl alcosol were made by Svedberg (see page 162). The former was black and the latter greenish black in transmitted light.

[4] Paal and Leuze: Ber., **39**, 1550 (1900); Gerasimov and Matveev: J. Russ. Phys-Chem. Soc., **62**, 839 (1930).

[5] Paal and Amberger: Ber., **38**, 1398 (1905).

[6] Gutbier and Hofmeier: Z. anorg. Chem., **44**, 227 (1905).

[7] Gutbier and Sauer: Kolloid-Z., **25**, 145 (1919).

[8] German Pats., 383,098 and 325,957.

[9] Ehrenhaft: Anz. Akad. Wiss. Wien, **39**, 241 (1902); Sitzber. Akad. Wiss. Wien, **112**, 182 (1903); *cf.* Billitzer: Ber., **35**, 1933 (1902).

[10] Phil. Mag., (6) **11**, 472 (1906).

Composition and Properties of Copper Sols

Composition

Copper sols formed by Bredig's method have been shown by x-ray analysis to be coated with a layer of copper oxide.[11] Both hydroxide and oxide have been detected chemically in this sol, the ratio $Cu(OH)_2/CuO$ decreasing with the time of passing the arc and with increasing *p*H value of the solution.[12] The conductivity of copper sols is distinctly lower than that of either silver or platinum sols. Evans[13] obtained values of 0.30–0.50 mho/cc, which were less than that of the conductivity water. This was attributed to adsorption of ions by the gelatinous copper hydroxide on the surface of the particles. According to Murray,[14] the conductivity of Bredig's copper sols is probably due largely to the saturated solution of copper hydroxide formed during the arcing process.

The positive charge on the particles of Bredig sols is due to preferential adsorption of copper ions by the oxide or hydroxide layer surrounding the particles. The hydroxyl ions are the contra ions which constitute the diffuse outer portion of the double layer.

No definite information is available concerning the composition and constitution of the relatively impure protected sols formed by reduction processes.

Stability of Sols

Effect of Radiations.—As already noted, chemically prepared copper sols formed in the absence of protecting colloids are quite instable. The Bredig sols are fairly stable at ordinary temperatures, but they are easily coagulated by the addition of electrolytes, by subjecting them to x-rays or the β-rays from radium, and by raising the temperature. Crowther[15] attributes the discharging action of the radiation to negative ions produced in the dispersing solvent by the ionizing agents. The action is therefore confined to positively charged sols. Moreover, since the negative ion produced by the ionizing agent appears to be the only active agent in the process, the effect is independent of the source of the ionizing radiation.

[11] Freundlich: Ber., **61**, 2219 (1928).
[12] Podrouzek: Chem. Listy, **20**, 403 (1926).
[13] Trans. Faraday Soc., **24**, 409 (1928).
[14] J. Chem. Soc., 1235 (1928).
[15] Phil. Mag., (7) **7**, 86 (1929); Crowther and Fairbrother; **4**, 325 (1927); *cf.* Bhatnagar, *et al.*; Z. Physik, **56**, 684 (1929).

Effect of Heat.—For a colloid like Bredig's copper sol to be stable, the particles must be sufficiently small that the Brownian movement keeps them from settling under the influence of gravity, and the charge on the particles must be sufficiently large that collisions do not result in coalescence of the particles to form larger aggregates. The mutual repulsion of oppositely charged particles does not come in until the particles are quite close together. Since it is now generally recognized that the outer layer of the electrical double layer is quite diffuse and may be several molecular diameters in thickness, the close approach of two particles will result in an overlapping of the outer layers so that the particles will possess an effective charge relative to one another and consequently will repel one another. But if the charge is sufficiently low or the Brownian movement sufficiently intense, the particles may touch and form an agglomerate in spite of the repulsion. One would expect the frequency of the effective collisions to be increased by lowering the charge on the particles by the addition of electrolytes or by increasing the intensity of the Brownian movement. The effect of electrolytes on the particle charge of hydrosols and hence on their stability has received extended study, and the effect of temperature alone on organosols has been considered by Svedberg and Inouye.[16] Recent investigations by Burton and his pupils[17] on a Bredig copper hydrosol show that, if samples of the sol are maintained at different high temperatures for a definite time interval, there exists one temperature below which the samples do not coagulate in a given time and above which they do coagulate. This temperature has been termed the "coagulation temperature" for the sol.

In the actual experiments the samples of sol were placed in a copper tube and sealed in a glass tube which was immersed in an electrically heated bath for a given time interval. Observations were made of the presence or absence of coagulation 24 hours after heating. Some results are given in Fig. 22. It is apparent that coagulation may be brought about by temperature alone. Moreover, the coagulation temperature decreases with increasing time of heating when the particle charge in each case is the same. Since the curve becomes asymptotic with the axis of time, the sol might be expected to remain stable indefinitely at room temperature. Finally, it was found that, by varying the charge on the particles by adding different amounts

[16] Kolloid-Z., 9, 153 (1911).

[17] Reid and Burton: J. Phys. Chem., 32, 425 (1928); Deacon: 34, 1105 (1930); Burton and Deacon: Colloid Symposium Monograph, 6, 77 (1928).

of potassium chloride, the coagulation temperature decreases with decreasing charge for the same time of heating.

In every case, heating the sol speeds up the process of coagulation so that eventually all the heated samples coagulate. The reason is that multiple particles are formed during the heating process, the more the higher the temperature, and that these agglomerates act as coagulation nuclei for smaller particles.[18]

The reason for the horizontal position of the curve in Fig. 22 is

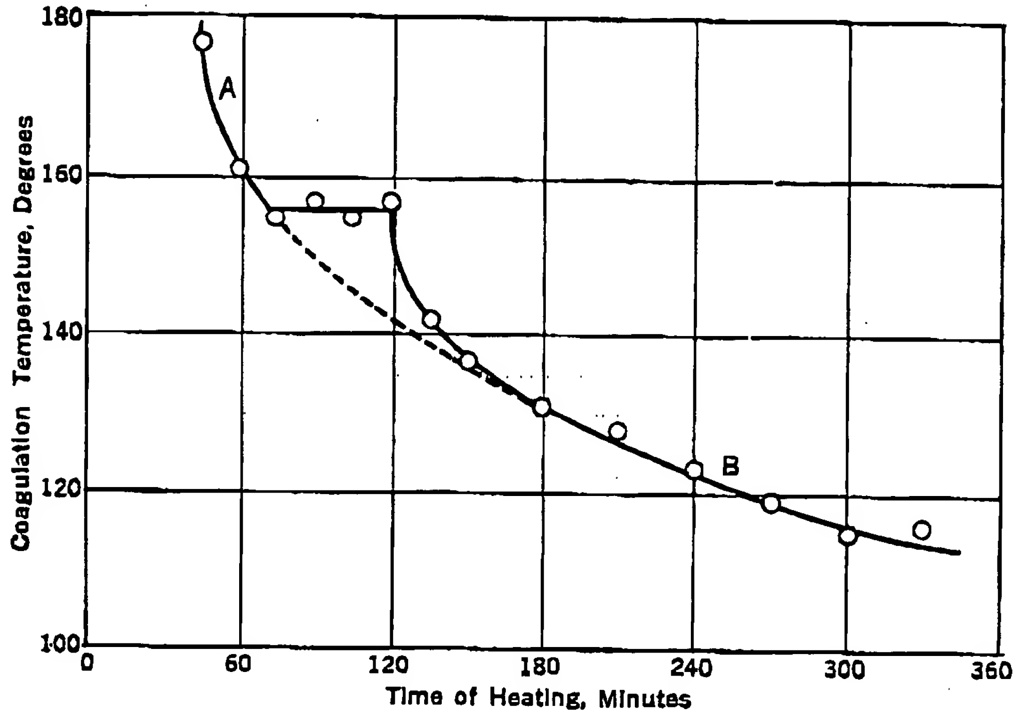

FIG. 22.—Effect of heat on the coagulation time of colloidal copper.

not at once apparent. It is suggested that at a temperature of 155° the cupric oxide or hydroxide on the particles is reduced to the cuprous state, thus disturbing the charge on the particles. If this be true, it is not obvious why the portions *A* and *B* apparently belong to the same smooth curve.

Effect of Electrolytes and Non-electrolytes on Organosols.—An alcosol of copper prepared by Bredig's method is sensitized and ultimately coagulated[19] by solutions of salts in various organic media miscible with alcohol, such as acetone, ether, and glycerin. The order of precipitating power of the salts is: lithium chloride < ammonium bromide < strontium chloride < mercuric chloride < aluminum chloride, which is the same as for a negative hydrosol. This

[18] Wiegner: Kolloid-Z., **8**, 227 (1911); Galecki: Z. anorg. Chem., **74**, 174 (1912); Müller: Kolloid-Beihefte, **26**, 257 (1928).

[19] Yajnik, Goyle, and Bhan: J. chim. phys., **27**, 386 (1930).

indicates that copper dispersed in ethyl alcohol is negatively charged. For a zinc sol in acetone, the cation is likewise the precipitating ion, the order of precipitating power of salts being: lithium chloride < sodium iodide < calcium nitrate < mercuric chloride < antimony trichloride. The coagulating action is due both to the lowering of the charge on the particle by the electrolyte and to the change in the solvation of the particle in the presence of the added non-electrolyte.[20]

Color

Like silver, colloidal copper exists in a wide variety of colors. Thus Paal and Steyer[21] obtained sols of the following colors: reddish brown, blue, ruby red, brown, olive, and green. Copper is used in place of gold in the preparation of a cheaper grade of ruby glass. In true copper ruby glass the particles are of ultramicroscopic dimensions; in opaque copper-red hematinon, they are microscopically visible; and in aventurine glass, they exist as spangles visible to the naked eye. From analogy with gold ruby glass one would expect the color of copper ruby glass to be due to colloidal copper. Williams[22] subscribes to this view, but Seger[23] attributes the color to colloidal cuprous oxide or copper silicate. Stokes[24] argues against the red color being due to colloidal copper on the ground that the most finely divided copper is blue; but his argument is not valid since it is the coarser particles which are blue. It is difficult to distinguish between colloidal copper and cuprous oxide in glass; but if the color is due to a copper silicate in solution, the glass should not scatter light as would a colloidal coloring agent.

Pharmacological Action

As already noted (see page 133), both colloidal silver and mercury are better bactericides than colloidal copper. The germicidal action of Bredig copper sol has been shown to be due exclusively to copper ions from cupric oxide and cupric carbonate formed in the presence of atmospheric gases.[25] Colloidal copper has been suggested

[20] *Cf.* Weiser and Mack: J. Phys. Chem. **34**, 101 (1930).
[21] Kolloid-Z., **30**, 88 (1922).
[22] Trans. Am. Ceram. Soc., **16**, 284 (1914).
[23] "Collected Writings," **2**, 731 (1902); Zulkowski: J. Soc. Chem. Ind., **16**, 441 (1897).
[24] "Mathematical and Physical Papers," **4**, 245 (1904).
[25] Kusunoki: J. Biochem. (Japan) **3**, 1 (1923).

for use in the treatment of cancer, but it has little apparent destructive action on tumor tissue.[26]

Solid Forms of Colloidal Copper

Copper Gel.—By electrolyzing in the cold a neutral or feebly basic 10% solution of copper acetate, Schutzenberger[27] obtained an extremely brittle, bronze-colored deposit which was very readily oxidized, had a higher electrical resistance than copper, and a specific gravity of 8 to 8.2, which is appreciably lower than that of the metal in mass. The deposit became like ordinary copper if heated rapidly to 100° or allowed to stand for some time in contact with dilute sulfuric acid. Schutzenberger believed this preparation to be an allotropic form of copper, and Benedicks[28] regarded it as a solid solution of acetic acid in ordinary copper. Briggs[29] showed, however, that the deposit was in reality a gel of the normal metal consisting of finely divided particles which were prevented from agglomerating into a dense mass by adsorption of a protecting film of gelatinous hydroxide or basic acetate from the partly hydrolyzed solution.

Briggs electrolyzed solutions of copper propionate, acetate, or formate in the presence of gelatin and obtained a finely divided deposit of gelatin-copper which underwent a striking "development" on immersion in a copper salt of a weak acid such as the acetate or propionate. The color changed from the original pale brown, through reddish purple, purple, and finally blue. The blue coloration was attributed to adsorption from the solution by the colloidal copper, of hydrous copper oxide or hydroxide, giving a colloidal copper-copper oxide adsorption complex similar to the gold-stannic oxide mixture, purple of Cassius.

Organic Condensing Agent.—Colloidal copper for use as a condensing agent is prepared by shaking zinc dust through a fine sieve into a thoroughly agitated, cold, saturated copper sulfate solution. The precipitate of finely divided copper is treated with dilute hydrochloric acid to remove any zinc, and finally is washed thoroughly with water.[30]

[26] Weil: J. Am. Med. Assoc., 61, 1034 (1913).
[27] Compt. rend., 86, 1265, 1398 (1878).
[28] Metallurgie, 4, 33 (1907).
[29] J. Phys. Chem., 17, 281 (1913).
[30] Cohn: "Arbeitsmethoden organisch-chemische Laboratorium," 360 (1903).

L Number	Hits	Search Text	DB	Time stamp
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L5             20 SEA (H3 O4 P)/MF
                  D 20
L6              1 SEA PHOSPHORIC ACID/CN
                  D
L7              1 SEA HYDROGEN PEROXIDE/CN
L8              2 SEA BLEACH
                  D 2
                  D 1
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                  D
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ON
     20 MAY 2002
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                  (HYDROGEN PEROXIDE OR BLEACH OR L3) AND (SODIUM CARBONATE OR
                  L9) AND (METHANOL OR ACETONE OR L10 OR L11) AND CITRATE
L13             4 DUP REM L12 (0 DUPLICATES REMOVED)
                  D 1-4
                  D 4 KWIC
L14             4 SEA COLLOID? (5A) (COPPER CITRATE)
                  D 1-4
                  D 4 KWIC
                  D 2 KWIC
                  D 1 KWIC
L15          1926 SEA COLLOID? (5A) COPPER
L16           374 SEA L15 AND (L2 OR COPPER SULFATE PENTAHYDRATE OR COPPER
                  SULPHATE PENTAHYDRATE OR PHOSPHORIC ACID OR L6 OR HYDROGEN
                  PEROXIDE OR BLEACH OR L3 OR SODIUM CARBONATE OR L9 OR
METHANOL
                  OR ACETONE OR L10 OR L11 OR CITRATE)
L17           347 DUP REM L16 (27 DUPLICATES REMOVED)
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                  D 1-36
                  D 36 KWIC
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